Uniform Molecular Flux in a Vertical Reactor with Pulsed Transition Regime Gas Flow

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UNIFORM MOLECULAR FLUX IN A VERTICAL REACTOR WITH PULSED TRANSITION REGIME GAS FLOW

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ABSTRACT

Pulsed-CVD technology accomplishes reactant delivery by timed injection of gas into a continuously evacuated reactor. The reactor conditions produced by this method are new to CVD processing. Seminal investigations to characterize the flow dynamics and transport phenomena for pulsed-transition regime flow are reported. Non-dimensional parameters for reactor design and process control are proposed, and the theory describing molecular impingement rate as a function of these parameters is presented. An experimental, industrial-scale reactor and experimental methods, including naphthalene sublimation, have been developed to investigate the flow dynamics. Pulses of known volume and pressure N_2 were delivered into the reactor at timed intervals, while monitoring the resulting reactor pressure and molecular flux field. Results demonstrate that uniform molecular flux can be achieved by Pulsed-CVD at pressures where steady flow would result in stable boundary layers, and thus non-uniform heat and mass transport fields at the substrate, and throughout the reactor.

INTRODUCTION

The purpose of CVD equipment is to deliver reactants to a heated substrate surface where a chemical reaction produces a solid material and gas or vapor products.[1] The relative rates of mass transport, surface reaction, nucleation, by-product removal, surface diffusion, and crystal growth determine the microstructure and properties of the thin film material. The critical requirement of any CVD technology is ensuring uniform deposition temperature and control of molecular flux at the substrate.

A unique CVD approach, called Pulsed-CVD, has demonstrated capability for direct control of thin film microstructure and thickness with uniform coverage.[2-5] Pulsed-CVD achieves process control through direct metering and timed injection of a precise volume of reactant gas into a continuously evacuated reactor. The strategy in running a reactor in this unsteady manner is to achieve relatively high molecular flux rates, uniform film thickness, and minimal impurities.

THEORETICAL APPROACH

A schematic for the Pulsed-CVD system with variable reactor volume, $V_R = \pi R^2 \cdot H_R$, is shown in Figure 1. A computer controls the timing of micro solenoid valves to fill the pulse supply volume with gas while valve A is open and B is closed, then inject the gas pulse into the reactor while valve A is closed and B is open. When the gas shot is injected into the reactor at the beginning of each pulse, a pressure spike, P_{max} results. Over the balance of the pulse cycle, the reactor is evacuated until the pump-down pressure, P_{min}, is reached. Continuous pulsed operation is achieved if the relationship between reactor volume, pump rate, pulse cycle time, and shot size are balanced so that P_{max} and P_{min} are constant for each pulse over the process. Given the ideal gas law, as in Eqn. [1], the number of molecules, n_i, pulsed into the reactor at the beginning of each pulse is controlled by setting the supply volume, V_s, and the supply pressure, P_s, at the supply temperature, T_s.

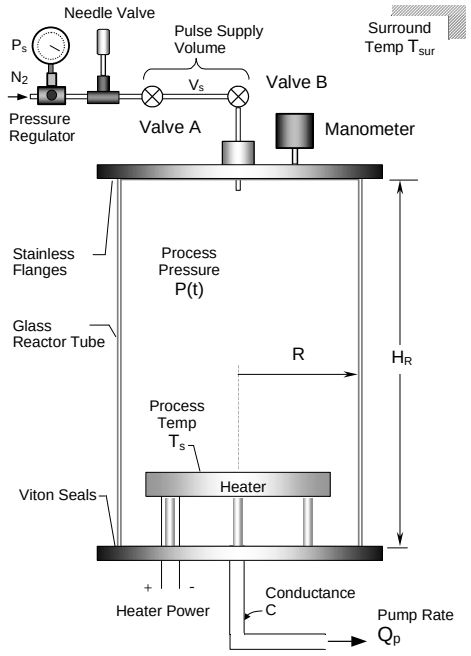

Figure 1. Schematic of the Pulsed-CVD reactor.

$$n_i = P_s V_s N_A / R_o T_s \qquad [1]$$

Where N_A is Avogadro's number, and R_o is the universal gas constant. Nitrogen was used as the gas for this study. Eqn. [1] is applied to the reactor at any time during the pulse cycle to determine the number of molecules, n(t), as a function of the reactor pressure P(t) at reactor gas temperature $T_R(t)$.

$$n(t) = P(t) V_R N_A / R_o T_R(t) \qquad [2]$$

As gas is injected into the reactor, it expands and cools, then is heated by the heater and surroundings. In this study, the heater was not powered, and the reactor gas temperature is assumed constant and equal to the ambient temperature, $T_R(t) = T_s = T_{sur}$.

A rotary vacuum pump with volume displacement rate, S_p, continuously evacuates the chamber at a rate, $Q_p = S_p C/(S_p+C)$, where C is the conductance of the vacuum tubing,

$C = 3.81(T/M)^{1/2}(D^3/L)$, after Knudsen. Eqn. [3] represents the molecular balance on the reactor volume at any time during the pulse cycle.

$$n_L dt - \frac{Q_P}{V_R}(n(t) - n_{\min})\, dt = d(n(t) - n_{\min}) \qquad [3]$$

Where n(t) is the number of molecules in the chamber at any time, n_{min} is the number of molecules at the pump-down pressure, P_{min}, and n_L is the molecular leak rate which is negligible compared to the pump rate. Rearranging and integrating from the start of a pulse, t = 0 to any time during the pulse cycle, t, and substituting Eqns. [1] and [2], the dimensionless reactor pressure, P*(t) is:

$$P^*(t) = \frac{P(t) - P_{\min}}{P_{\max} - P_{\min}} = \exp\left(-\,{}^{t}\!/\!_{\tau}\right) \qquad [4]$$

where τ is the time constant of the reactor, and P_{max} is the peak pulse pressure:

$$\tau = {}^{V_R}\!/\!_{Q_P} \qquad P_{\max} = P_s\left(\frac{V_s}{V_R}\right)\left(\frac{T_R}{T_s}\right) + P_{\min} \qquad [5]$$

It is proposed that the gas dynamics models from rarified gas theory apply to the flow in Pulsed-CVD, and that this flow field is best modeled as transition regime flow.[6,7] Although the pressure range for Pulsed-CVD would be considered viscous if the flow conditions were steady, the principle conditions of viscous flow theory are not the dominating factor in pulsed flow. Viscous flow theory describes gas flow in the direction of a pressure gradient where the velocity decreases uniformly from the axis of the flow until it reaches zero at the wall. Each layer of gas parallel to the wall, in the direction of flow exerts a tangential force on the adjacent layer, through momentum transfer associated with intermolecular collisions. Molecular flow describes the state where the mean free path exceeds the distance between walls in the direction of flow, so that momentum transfer is only between gas molecules and the walls. Viscous flow exhibits organized momentum transfer from the free flow stream to the walls, while molecular flow exhibits no momentum transfer. In viscous flow the boundary layers formed along walls dominate the mass and thermal transport mechanisms. In molecular flow, mass and thermal transport are on a molecular scale, and thus very small.

Neither of these states accurately describes pulsed low-pressure flow by instantaneous injection into a large evacuated vessel. It is proposed that the flow

dynamics in Pulsed-CVD are appropriately modeled as transition regime phenomena. The mass transfer processes in Pulsed-CVD are dominated by random molecular motion induced by the unsteady nature of the process. Thus the rarified gas theory is used to describe the flow dynamics, and the experimental evidence will verify the transition regime hypothesis by demonstrating mass transport rates equivalent to viscous conditions. However, the mass transport rates for Pulsed-CVD are uniformly distributed throughout the flow field, while equivalent viscous flow mass transport rates vary widely throughout the flow.

From the familiar Maxwell-Boltzmann relations,[8] we have expressions giving the instantaneous parameters for the gas molecules in the reactor at any point during the pulse cycle. The root mean square molecular velocity, v_{N2} is a function of gas temperature only:

$$v = \sqrt{3R_o T_R / M} \qquad [6]$$

Where M is the molecular mass. For N_2 the molecular speed is about v_{N2} = 4.5 x10^4 cm/s. The molecular incidence rate, ϕ(t), is given by:

$$\phi(t) = \frac{P(t)}{\sqrt{2\pi M R_o T_R}} \qquad [7]$$

And the mean free path, λ(t), is given by:

$$\lambda(t) = R_o T_R \Big/ \left(\sqrt{2}\pi N_A \xi^2 P(t)\right) \qquad [8]$$

Where ξ is the molecular diameter. The mean free path at P_{min} is in the range of λ_{max} = 12 mm. Given the molecular speed and the mean free path at the time of injection, it is proposed that the gas injected into the reactor disperses uniformly into the reactor volume within 0.1 sec.

One measure of the dominant process in the flow dynamics during the pump-down process is the ratio of the number of intermolecular collisions, X = $nV_R v_{N2}/\lambda$, to the number of molecule-wall collisions, N = ϕA_R.

$$X/N\,(t) = 4\sqrt{2}\pi n(t)\xi^2 \left\{\frac{V_R}{A_R}\right\} = \frac{4\pi\sqrt{2}\xi^2 N_A}{R_o T_R}\left\{\frac{V_R}{A_R}\right\} P(t) \qquad [9]$$

When the ratio, X/N, is greater than 20, the flow is considered viscous, and when X/N is less than 0.2, the flow is molecular. The range of X/N between 0.2 - 20 represents transition regime flow.[9]

For Pulsed-CVD, over the time interval $\Delta t = t_p$ equal to one pulse cycle, the total flux per unit surface area is found by substituting Eqn. [4] into Eqn. [7] and integrating over the pulse cycle:

$$J_P = \left\{ \frac{N_A}{\sqrt{2\pi M R_o T}} \right\} \left[P_{\min} t_p + \tau (P_{\max} - P_{\min}) \left(1 - e^{-t_p/\tau} \right) \right] \qquad [8]$$

Using the definition for $J = \phi t_p$, a non-dimensional pulsed molecular flux, J_P^*, can be defined:

$$J_P^* = \frac{J_P - J_{\min}}{J_{\max} - J_{\min}} = \frac{\tau}{t_P} \left(1 - e^{-t_P/\tau} \right) \qquad [9]$$

EXPERIMENTAL RESULTS

Two sets of experiments were conducted to study the pulsed reactor operation, and to compare the flow dynamics for pulsed flow and comparable steady flows, which would have the same molecular flux rate to the deposition surface. Two capacitance manometers with overlapping ranges (MKS622A, 626A) were used to measure reactor pressure. The pressure data in Figure 2 gives a curve fit to Eqn. [4] of τ = 4.4 sec, which is in good agreement with the reactor parameters from Eqn. [5] which gives τ = 4.5 s. If the pulse cycle time is too short, the reactor does not return to the pump-down pressure before the next shot is injected, and the total reactor pressure climbs steadily throughout the process. If the pulse cycle time is longer than necessary, the process time can become un-necessarily long.

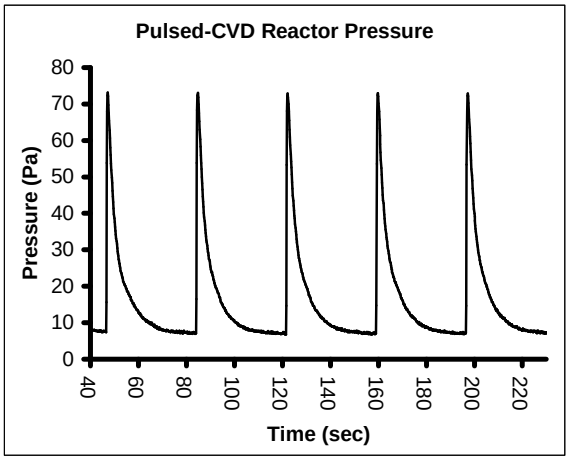

Figure 2. Reactor pressure over several pulse cycles. Pulse cycle time, t_p=38 s, reactor volume V_R= 4.45 lit, pump rate S_P=2.5 lit/s, conductance, C=1.64 lit/s, injection volume, V_s=1400 mm^3, supply pressure, P_s=150 Pa(g).

The nature of the molecular flux field in the reactor were ascertained by using a naphthalene sublimation technique, usually employed in viscous flow experiments to measure, indirectly, the convective heat transfer coefficient by invoking the heat and mass transfer analogy.[10] Small cylinders (9.5mm dia., 14mm ht.) of naphthalene were cast with a thin wire holder embedded in one end. The surfaces were smoothed, and a thin wire frame was used to suspend the samples at various positions in a Pulsed-CVD reactor with volume V_R = 4.45 lit. The first experiment measured the sublimation rate at the pump-down pressure, 7.5 Pa, which is equal to the vapor pressure of naphthalene at 20^{o}C. The second experiment measured the sublimation rate with pulsed gas injection of 1400 mm^3 at t_p = 38 sec intervals, resulting in P_{max}= 73 Pa, and P_{min} = 7.5 Pa. The molecular flux per pulse, $J_p = \Sigma\phi_i t_i$ was calculated using Eqn. [7], the pressure data, and the sampling time, t_i = 0.15 s, giving J_P = 4.79E23 molec/m^{2}pulse. Using Eqn. [7] the equivalent steady pressure over a 30 second pulse period would be achieved at a pressure of 17.7 Pa. During the first five seconds of the pulse, the flux rate is very high, equivalent to a steady pressure of 48 Pa.

Napthalene sublimation rates were measured for two steady flow experiments. Nitrogen gas flow was controlled by micrometer valve on the gas inlet. Figure 3 shows the results of sublimation tests run at constant vacuum, pulsed flow, and steady flow at 10 Pa and at 50 Pa. The evidence of viscous flow effects, variable sublimation rates at different reactor positions, are evident as expected under steady flow conditions at 50Pa (X/N = 110). However, in the pulsed reactor, with X/N ranging between 81 and 800, the sublimation rate is constant throughout the reactor.

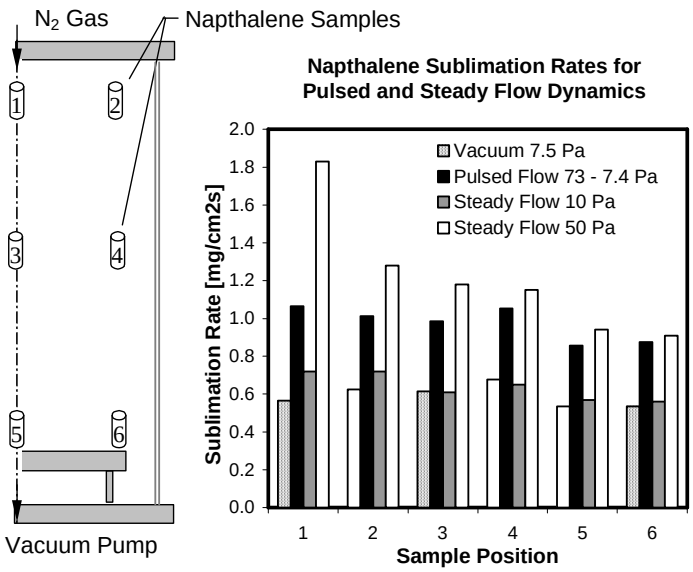

Figure 3. Positions of naphthalene sublimation samples in the P-CVD reactor. Sublimation rates for constant vacuum of 7.5 Pa, pulsed flow with t_p = 30 sec, τ = 4.3 sec, P_{max} = 73 Pa, P_{min} = 7.5 Pa, and for steady flow at 10 Pa and 50 Pa.

CONCLUSION

In this study, the operational and performance parameters for Pulsed-CVD are proposed, including the process time constant, τ, the ratio of reactor volume to rector pump rate, and the pulse flux, J_p^*, which is the cumulative molecular flux over one pulse cycle. The theoretical development of transition regime flow dynamics and mass transport models per pulse cycle were based on rarified gas theory applied to disordered, unsteady, compressible viscous regime flow. Experiments were conducted to determine empirical relationships between the design and operating parameters, and to verify the transition regime flow dynamics through evidence of a uniform flux field achieved by pulsed operation. This experimental work required development of a naphthalene sublimation technique to compare the relative molecular flux field in the reactor for pulsed and steady flow. It was determined that operation with the pulse cycle time greater than or equal to 4τ provides regular, repeatable pulsing cycles. Sublimation evidence indicates that pulsed operation produces equivalent molecular flux rates to viscous flows, but with uniform flux field throughout the reactor and on the substrate surface in particular.

REFERENCES

1. C.E. Morosanu, *Thin Films by Chemical Vapor Deposition*, Elsevier, Amsterdam, (1990)
2. S. Krumdieck, and R. Raj, *J. Amer. Ceram. Soc.*, 82[6] 1605-07 (1999)
3. S.P. Krumdieck, PhD Dissertation, Univ of CO at Boulder (1999)
4. S. Krumdieck, *Acta Mater.*, **49** 583-588 (2001)
5. S. Krumdieck, and R. Raj, *Adv. Mat. CVD*, **7 No. 2** 85-90 (2001)
6. S. L. Thomson and W.R. Owens, *Vacuum*, **25 No.4** 151-156 (1974)
7. S.F. DeMuth and J.S. Watson, *J. Vac Sci. Technol. A*, **4 No.3** 344-347 (1986)
8. A. Roth, *Vacuum Technology*, North-Holland, Amsterdam (1990)
9. P.R. Souza Mendes, *Exper. Thermal And Fluid Sci.*, **4** 510-523 (1991)